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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Method for Treatment and Recycling of Pulp Mill Bleach Plant Effluents

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**Canada**

Abstract

The invention relates to a method for treatment and recycling of pulp mill bleach plant effluents. Chlorine-containing chemicals are separated from the fluid obtained from the first bleach stage (DC) implemented with these chlorine-containing bleach chemicals on pulp (2) that has been washed (W) and partially dewatered (P1) whereby the pulp (3) from the mentioned bleach stage (DC), with chlorine-containing bleach chemicals, is dewatered (P2) up to about the same dryness of at least 25 % and at most 35 % as for the mentioned thereto incoming pulp (2) and whereby the fluid from the second dewatering (P2) is recycled to the bleach stage (DC) and the outcoming fluid (9) from the bleach stage (DC) is evaporated (EV) through indirect heating with condensing vapour obtained through recompression of vapour stripped in the evaporation. The dewatering (P1, P2) is preferably performed by pressing out the liquid from the pulp (2, 3) and the evaporation (EV) in several stages connected in parallel or in series at a temperature below 70°C.

Method for treatment and recycling of pulp mill bleach plant effluents

The present invention relates to a method for treatment and recycling of pulp mill bleach plant effluents. In particular, the present invention relates to a method for separation of chlorine-containing chemicals from the fluid obtained from the first bleach stage performed with these chlorine-containing bleach chemicals on washed and partly dewatered pulp.

Thus the purpose of the present invention is to achieve a method for treatment and recycling of the effluents caused in pulp bleaching so that the effluent is separated into separate fractions, of which one fraction can be recycled to the mill's chemical recovery system and another fed to equipment with which contaminating substances can be separated from the fluid, which then can be re-utilized in the process and the contaminants transformed into a state harmless to the environment.

In production of fully bleached pulp according to the sulphate or sulphite method there is no other choice than to use chlorine-based oxidating bleach chemicals. These bleach chemicals are mostly molecular chlorine, chlorine dioxide and hypochlorite. In the bleach process the chlorine, as a result of chemical reactions, is mainly transformed into chloride ion, but about 10 % of the chlorine is bound to organic material. The bleaching of chemical pulp is divided into stages with different chemicals added. Partly the chlorine compounds are used in the first bleach stage as a reactant to degrade lignin contained in the unbleached pulp and partly in the last stages to eliminate chromophor groups from the pulp and thus give it its final brightness. All oxidative degraded lignin is not water soluble in the acid environment of the first bleach stage. In the second bleach stage degraded lignin is therefore extracted from the pulp using sodium hydroxide, at the same time as a further oxidative lignin degradation is carried out with oxygen and possibly hydrogen peroxide.

In the first bleach stages principally the residual lignin in the pulp is extracted, which thus is contained in the waste liquors from these bleach stages. For example in production of fully bleached softwood kraft pulp, the extracted organic substance is 3-5 % of the pulp production. This organic substance has a high biologic oxygen demand (BOD) and a very dark colour and it contains the major part of the chlorinated organic material, measured for example as adsorbable organic halogen (AOX). Partly the chlorinated organic material is high-molecular with a more or less unknown composition, and partly low-molecular. The low-molecular part contains substances that have turned out to be toxic, mutagenic and having a tendency to bioaccumulate in the ecological system.

The bleach plant effluents are so far discharged to a water recipient, mostly though via a process-external effluent treatment in an aerated lagoon or activated sludge plant. The effluent treatment efficiently reduces the BOD concentration but not the biologically inactive organic material. Even the most efficient biologic effluent treatment plants are capable of reducing the total concentration of organic material and also the concentration of organically bound chlorine with only 50 %. Thus the bleach plant effluents constitute a considerable environmental dilemma to the pulp mills.

Various methods have been explored to solve this problem. What mainly has been examined is the possibilities to recycle the bleach plant effluents within the mills' chemical recovery systems for destruction of the organic substance for example in the recovery boiler of the kraft pulp mill. Well-known is the mill scale trial carried out at Great Lakes Paper Co's pulp mill in Thunder Bay, Canada ten years ago. The difficulty in recycling bleach plant effluents is that the chlorides in the water are concentrated in the process thus causing process failures and accelerated corrosion in the equipment. To solve this problem, evaporation of white liquor and a partial crystallization of sodium chloride was introduced in the above-mentioned pulp mill. At this stage, however, the

chloride-containing black liquor had already passed through the liquor evaporation plant and been combusted in the recovery boiler. Great difficulties forced the mill to return to the common praxis of discharging the bleach plant effluents to an external water recipient.

Well-known is also the ultrafiltration technique for treatment of effluents containing high-molecular substance. In this case the effluents flow over microporous membranes, which let through low-molecular material but retain high-molecular material. This technique is used for example at Taio Paper Co in Japan for separation of the high-molecular substance from the effluents of the second (alkaline) bleach stage. The major part of the organic material as well as the chloride ions in the effluents from the bleach stage where chlorine-containing bleaching agents are used do pass through the commercially relevant membranes, though. Therefore this technique is not suitable for mill scale treatment of chlorine-containing bleach plant effluents.

With presently existing technology it is thus impossible to separate the contaminants in the bleach plant effluents with process-internal measures so that the water could be recycled into the process and the contaminants destructed in a way not harmful to the environment. This can be seen from the fact that all the world's pulp mills today discharge their bleach plant effluents to an external water recipient.

The present invention relates to a new method for enabling partial or total recycling of bleach plant effluents through process-internal interconnecting of individually known devices and with simultaneous transforming of both chlorinated and non-chlorinated organic substance extracted in the bleach plant into a state harmless to the environment.

The primary characteristics of the invention appear from claim 1 of the patent claims presented below.

According to a presented type of the invention, the pulp is dewatered by pressing out the liquid from it, with for example a screw press, preferably to a dryness of 25-35 w.p.

The fluid discharged from the bleach stage can be evaporated in several parallel or consecutive stages preferably at a relatively low temperature below 70°C.

The condensate achieved through recompression of the evaporated vapour is preferably completely or partially recirculated from the evaporation to some subsequent bleach stage for use as wash liquor. The evaporation is preferably performed up to a dryness high enough to let the evaporation residual be dried and combusted to inorganic material.

Below the present invention is described more in detail with reference to enclosed drawings, in which figure 1 shows a connection diagram of a typical modern pulp bleaching plant in a simplified manner, whereas figure 2 shows a connection diagram for application of the method according to the present invention.

To an expert it is clear that the description and drawings only constitute an example of the application of the invention and thus not include all the alternatives covered by the patent claims.

The typical connections of a modern pulp bleaching plant are shown in figure 1 in a simplified manner. Here W indicates the wash room, in which the waste liquor from the digesters is separated from the unbleached stock. Generally the wash room consists of several counter-current wash filters or combined devices where counter-current washing can be achieved. The washed brown stock is taken to a process stage with oxygen delignification, in figure 1 indicated with O. This stage is omitted in many applications and is not essential to this invention. After a possible oxygen delignification with a subsequent washing stage, the brown stock is taken to the bleach plant. The bleaching is performed in four or five consecutive bleach stages.

Each one of these consists of devices for dosing of bleaching chemicals into the pulp suspension, a bleach reactor to achieve enough retention time for the reaction, and a device for washing of the stock. In figure 1 the first bleach stage is indicated with DC. Chlorine gas and chlorine dioxide are fed to this stage in various proportions. After washing, which normally leads to a pulp concentration of 10-12 % after the washing stage, the stock is fed on to the alkaline bleach stage, in figure 1 indicated with EO. Sodium hydroxide and often also oxygen gas are fed to this stage. After the chemical treatment, the stock is also washed in the EO stage resulting in a pulp concentration of 10-12 % after the washing stage. Now the stock is taken to final bleaching in the bleach stages indicated with D1, E and D2. Normal chlorine dioxide is fed to D1 and D2 and sodium hydroxide to E. In some cases the E stage is omitted, which is not essential to this invention.

In figure 1 some main flows between the separate devices are indicated. The flows indicated with 1-4 show the pulp suspension flowing through the plant, flow 1 is the brown stock suspension from the digester house and flow 4 the bleached pulp suspension. Each bleach stage contains a pulp washing stage and figure 1 shows the main flows of wash liquor, which transport dissolved solids in the bleach plant. 5 and 10 indicate clean washing water - often white water from the bleached stock cleaning - coming to the bleach plant. 6 is wash liquor discharged from the D2 stage and containing chlorine substances and relatively small quantities of extracted organic material, a liquor which is fed as incoming wash liquor to the D1 stage, the outgoing wash liquor of which is indicated with 8 and often used as wash liquor in the DC stage. Wash liquor 9 from this stage is heavily contaminated by both organic material and chlorine substances, and in conventional bleach plants it is taken to an acid waste water canal.

In conventional bleach plants fresh water is used for washing water 10 to the E stage. 12 is wash liquor discharged from this stage, a liquor which is fed as

incoming wash liquor to the EO stage, the outgoing wash liquor of which is indicated with 13 and heavily contaminated and, in conventional bleach plants, taken to an alkaline waste water canal. The waters in the acid and alkaline waste water canals are combined and taken via process-external effluent treatment to an external recipient.

This description of the wash liquor distribution in the bleach plant does not include the flows of wash liquor leading from one washing stage to the preceding stage, because this wash liquor only displaces the water contained in the pulp and does not essentially mix with the wash liquor discharged from this stage. Furthermore there is an internal fluid circulation within the bleach stages for transport and formation of the filter cake in some washing devices. This circulation has not been indicated in figure 1 and is unessential to this invention.

The method according to this invention is described with figure 2. This method differs from the known process as described above primarily with respect to three new devices that have been introduced in the bleach plant, in figure 2 indicated with P1, P2 and EV. P1 and P2 are dewatering devices, with which the consistency of the pulp suspension to and from the DC stage is raised above the normal, for example from 10-12 % to 25-35 %. The purpose of these devices is to reduce the volume of water brought with the pulp to and taken out from the DC stage. The pressed out liquid is returned to the preceding stage and used there as dilution liquor. Since the carryover of dissolved solids in the fluid is proportional to the volume of transferred fluid, the raise of the pulp consistency in P2 will reduce the ~~carryover of chlorine-containing material to the EO-~~ stage, especially as a suitable quantity of the discharge water from the EO stage is used to displace the major part of the chlorine-containing discharge to the normal washing device of the DC stage. When the carryover of chlorine-containing material to the EO stage has thus been considerably eliminated, wash liquor flow 13 from this stage can be recycled to the mill's

chemical recovery system. According to the example in figure 2 this would be implemented by combining the flow in question with discharge flow 14 from the oxygen delignification to flow 15 to be used in a suitable manner together with the normal washing water flow 16 to the wash room W.

To balance the water flows in the three last stages of the bleach plant, a certain overflow 7 of wash liquor from the D1 stage can occur. This is then led to the waste water canal. The concentration of organic material in the discharge water from the final bleach stages is, however, considerably lower than from the first two bleach stages, and therefore such an overflow - if it occurs - does not reduce the value of the invention as method for cleaning the bleach plant effluents.

The function of the dewatering device P1 is to reduce the incoming water to the DC stage. If the water volume in flow 2 to the DC stage is bigger than the water volume in flow 3 out from the stage, the difference will be discharged in discharge water flow 9. To considerably reduce this water volume, which would load device EV, the dewatering device P1 is needed.

The devices P1 and P2 can be separate devices, for example well-known screw presses, or their function can be integrated with the washing device as in well-known pressure washers.

The device EV is an evaporation unit. In this unit added discharge water is evaporated. Heat is taken from condensing vapour to evaporate the water in the discharge and the vapour thus formed is compressed to a higher pressure and used as a source of heat for evaporation of more water. The condensing vapour and the boiling discharge are separated by a non-permeable heat-conducting membrane. The condensate formed when the vapour is condensed contains no non-volatile compounds and is thus free from salts and also all organic material with cooking temperatures above the temperature at which the evaporation takes place in the device.

The device EV is thus a well-known, e.g. from patent application FI 79948, evaporation device. EV can consist of such a device, but in general several devices of this type are needed, connected in parallel or in series. These types of connecting are known. For this invention it is, however, suitable that the evaporation unit functions through thermal recompression, thus having no continuous vapour demand. Further it is preferable but not necessary that it operates at a low temperature level, typical evaporation temperatures being below 70°C, to avoid unnecessary heating of the discharge water and to prevent evaporation of organic material and stripping of hydrochloric acid. This means that the device in that case operates at a pressure below atmospheric pressure and that the pressure differences over the non-permeable heat-conducting membranes in the device are small. The membranes can therefore be thin and made for example from plastic material.

With the device EV the heavily contaminated and chlorine-containing discharge water flow 9 can thus be divided into an essentially clean water flow and a concentrate flow. The concentration of dissolved solids in this flow is typically above 10 %. The purified water fraction is clean enough to be used as process water in the mill, according to figure 2 for example as wash liquor flow 10 to the E stage of the bleach plant (or the EO stage if there is no E stage). In some cases stripping of hydrochloric acid gas can take place together with the evaporation of the water, when the concentration of dissolved solids in the evaporation becomes higher. To avoid any disturbing return of chlorine to the bleach plant, the device EV can consist of evaporation units connected in series in the water section, all operating with recompression of stripped, condensed water vapour but with different concentration levels of the solution to be evaporated. The condensate coming from the devices operating at a high concentration level and being contaminated with chloride ions but not with organic material, is discharged to the waste water canal, and only the non-contaminated condensate is returned to the bleach plant.

The concentrate contains the chlorine compounds, mainly chloride ions, and the non-volatile organic material. It is taken out as flow 17 from the device EV. This concentrate is passed to the incinerator IN, where it is dried and combusted using the air stream 18. When the acid chloride-containing concentrate is dried, a stripping of hydrochloric acid gas takes place. This hydrochloric acid can be absorbed into an added flow 21 of water or liquor solution. Stripped hydrochloric acid is then contained in the outgoing absorption water 22. The organic material is completely combusted and it passes out as carbon dioxide and water vapour with the flue gas stream 19 from the incinerator. All organically bound chlorine is transformed into inorganic state and tanken out as ash stream 20 from the incinerator. The technique of incinerating wet material is well-known and there are many variants for its implementation, e.g. the one described in U.S. Patent 4 159 682. Which one of these that would be used is not essential to this invention.

What is claimed is:

- 1 A method of separating chlorine-containing chemicals from the fluid obtained from the first bleach stage (DC) implemented with these chlorine-containing bleach chemicals on pulp (2) that has been washed (W) and partly dewatered (P1), whereby the pulp (3) from the mentioned bleach stage (DC), with chlorine-containing bleach chemicals, is dewatered (P2) up to about the same dryness of at least 25 % as for the mentioned thereto incoming pulp (2) and whereby the fluid from the second dewatering (P2) and the outgoing fluid (9) from the bleach stage (DC) are evaporated (EV) through indirect heating with vapour obtained through recompression of vapour stripped in the evaporation.
- 2 The method of claim 1, wherein the pulp is dewatered (P1, P2) to a dryness of 25-35 w.p.
- 3 The method of claim 1 or 2, wherein the pulp (2, 3) is dewatered (P1, P2) by pressing out liquid from it.
- 4 The method of claim 1, 2 or 3, wherein the evaporation (EV) is performed in several stages connected in parallel or in series.
- 5 The method of claim 4, wherein the evaporation (EV) is performed at a temperature below 70°C.
- 6 A method of some of the preceding claims, wherein the condensate (10) achieved through recompression of the stripped vapour is recycled at least partially from the evaporation (EV) to some subsequent bleach stage (E) for use as washing water.
- 7 A method of some of the preceding claims, wherein the evaporation (EV) is performed up to such a dryness that the evaporation residual (17) can be dried and incinerated (IN) to inorganic material (20, 22).

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8 A method of some of the preceding claims, wherein the fluid from the second dewatering (P2) is recycled to the mentioned first bleach stage (DC) with chlorine-containing bleach chemicals.

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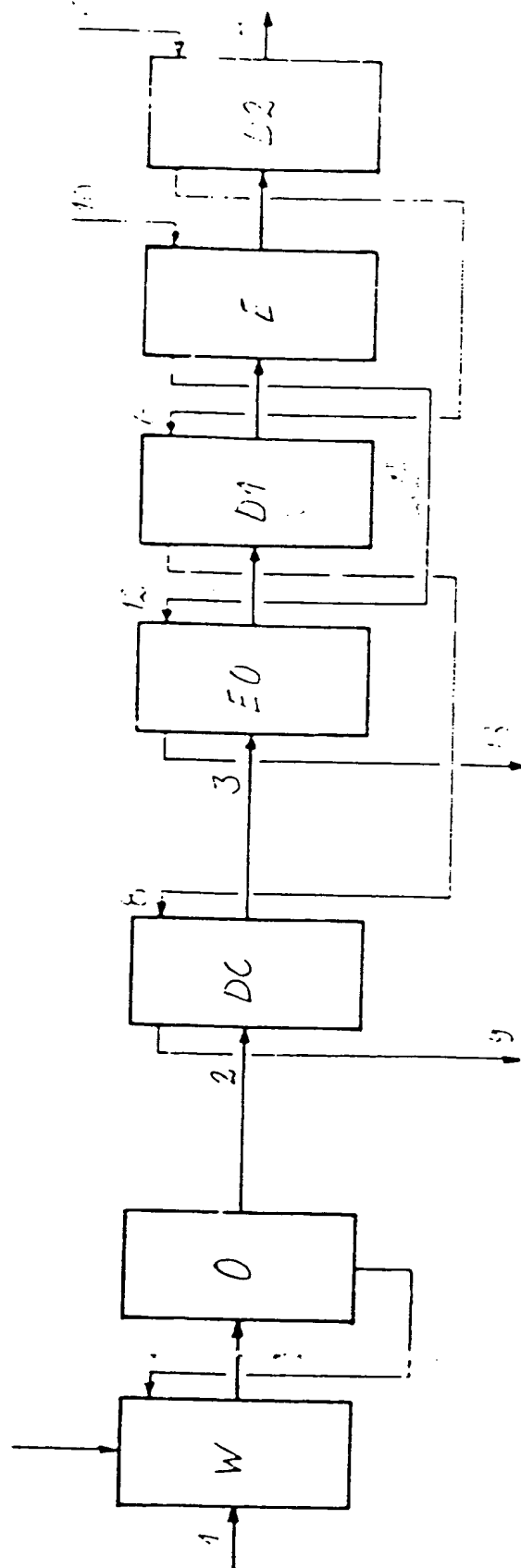


Fig. 1

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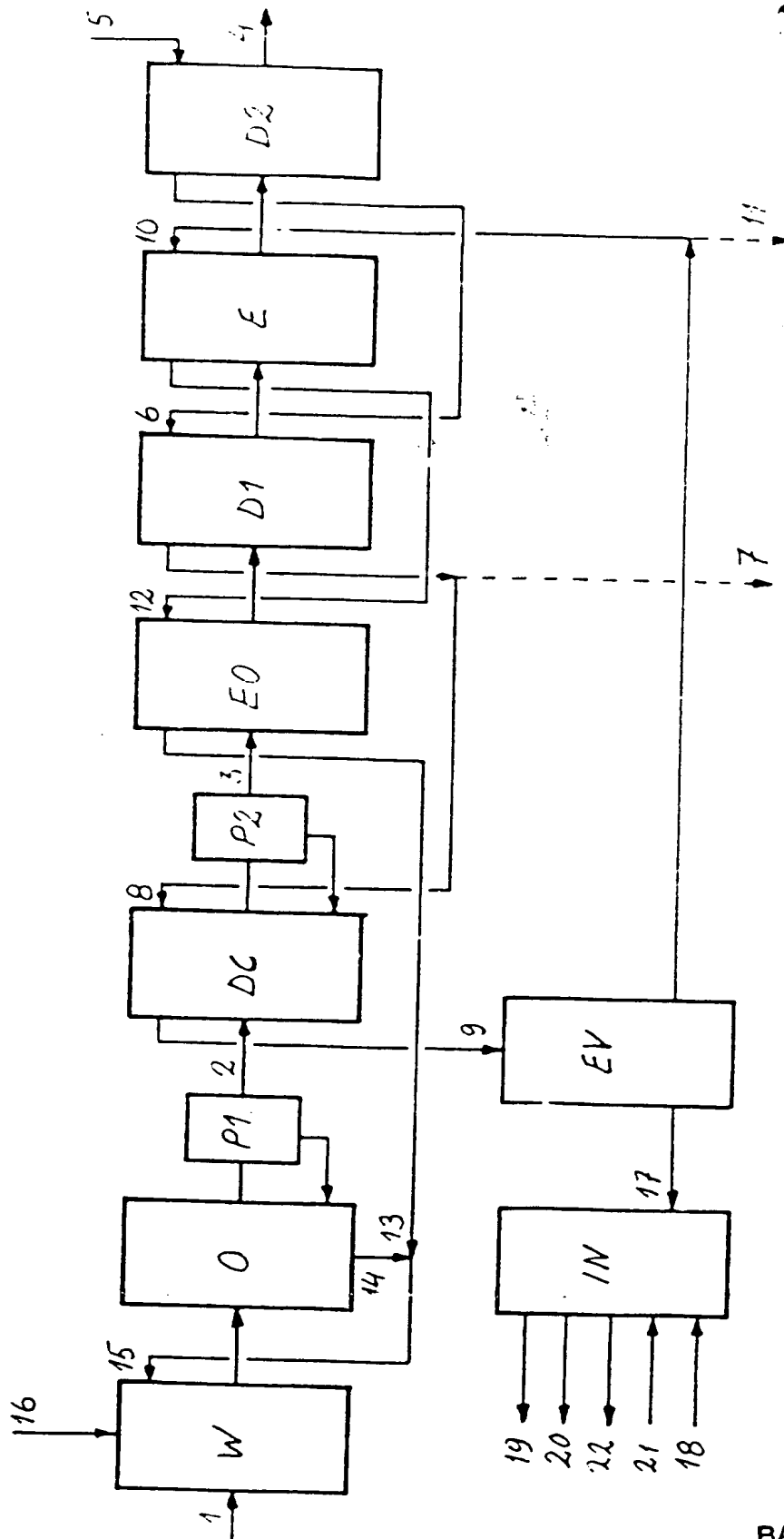


Fig. 2

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